SUPERCRITICAL FLUID METHODS FOR COAL EXTRACTION, SEPARATION, AND ANALYSIS

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INTRODUCTION

Supercritical fluids are attracting increased interest for media for coal liquefaction and gasification, the basis for new separation techniques, and in new analytical techniques for the separation and characterization of coal-derived products. On-going research at Pacific Northwest Laboratory (PNL) is examining a range of supercritical fluid applications, including their use as a reaction media for coal liquefaction and for separation of fuels and coal-derived products. Other programs at PNL are studying the applications for analysis of fuel samples using supercritical fluid chromatography (SFC), the new technique of direct fluid injection-mass spectrometry (DFI-MS), and their combination (SFC-MS). In this report we will present an overview of the range of supercritical fluid applications at PNL related to coal and fuel separation and characterization.

EXPERIMENTAL

Two similar instruments have been utilized in our supercritical fluid studies to date. The first is a micro-scale supercritical fluid extraction/reaction facility designed to allow the rapid study and characterization of the fluid phase under a wide range of conditions. The second instrument is utilized for analytical studies which include direct fluid injection-mass spectrometry[2] and capillary column supercritical fluid chromatography-mass spectrometry[3]. The instrumentation has been described previously[1-3]. Figure 1 shows a schematic illustration of the DFI-MS instrumentation. Instrumentation for direct supercritical fluid extraction involves replacement of the injector by an extraction cell containing the material to be studied, while SFC-MS involves addition of a suitable open tubular capillary column between the injector and DFI probe[3].

RESULTS AND DISCUSSION

The direct fluid injection (DFI) method allows any compound soluble in a supercritical fluid to be transferred to the gas phase for ionization using conventional methods[2]. Recent work at PNL has led to the design and development of Supercritical Fluid Extraction-Mass Spectrometer (SFE-MS) utilizing the DFI concept. The DFI method has the following advantages: quantitation is straightforward; the process is applicable to essentially any compound; various CI reagents may be selected to vary the degree of spectral complexity (fragmentation); and the technique is inherently sensitive.

The DFI probes have been designed to couple with the direct probe inlet of a modified "simultaneous" chemical ionization-electron impact (CI-EI) ion source[1-3]. Chemical ionization provides both excellent sensitivity and flexibility due to the potential for the addition of different or mixed CI reagent gases. For cases where additional structural information is necessary for identification one can use either more energetic mixed CI reagents or the collision-induced-dissociation (CID) capability of the tandem quadrupole analyzer. The use of CI analysis for coal extraction is particularly attractive since the gentle ionization mechanism produces primarily protonated molecular ions (MH^+), which allows information on the molecular weight distribution to be obtained directly from the mass spectra. The DFI interface has also allowed the first practical supercritical fluid chromatography (SFC) -mass spectrometer instrumentation to be developed[3]. The combination of the selective extraction from substrate materials and detection with more selective collision induced dissociation tandem mass spectrometric methods (e.g., MS/MS) offers a particularly effective rapid analytical method for complex coal extraction and related coal-derived mixtures.

The last few years have seen a dramatic growth in the application of supercritical fluid extraction methods to a variety of extraction, separation, and process areas. The strong and often selective solvating power of supercritical fluids under controlled conditions often allows extraction of specific compounds (e.g., caffeine from coffee, PCB's from transformer oils, etc.) from complex matrices, as well as efficient extraction of a wide range of compounds under more severe conditions. Under more extreme conditions the "extraction" process for materials such as coal is undoubtedly a combination of chemical reactions resulting in breakdown of the complex matrix combined with the extraction-distillation process of the supercritical fluid.

The present methods for direct analysis of coal supercritical fluid extraction (SFE) processes involves the continuous removal of a small sample from an extraction cell for direct mass spectrometric analysis. A high pressure syringe pump, modified for pressure regulation, is used to maintain the desired pressure in the extraction cell. The extract is transported using a 25 cm length of 100 μm I.D. platinum-iridium tubing through the DFI probe which is maintained at the same temperature as the extraction cell. The entire sample line volume is approximately 2 μL and, for our typical flow rates of 10-30 μL/min, the time from extraction to analysis is less much than one minute. Fluid from the cell is injected directly into the CI region of a "simultaneous" dual EI-CI source where a constant pressure is maintained. The mass spectrometer, programmable pressure regulated pump, oven temperature controller and data acquisition hardware are all interfaced for complete computer control[3].

The supercritical fluid phase reaction or extraction process can be studied under both nonisothermal and nonisobaric conditions. Small extraction cell volumes allow evaluation of compounds extracted as a function of pressure for the determination of "threshold pressures" for the solubility of individual components. The effects of catalysts can be studied in the extraction cell or a subsequent separate reaction cell. Large reaction volumes allow one to observe the fluid phase processes as a function of either temperature or pressure, where the parameter is varied in some known fashion with time. For large reaction cells (>50 mL) the actual loss due to mass spectrometric sampling (<25 μL/min) can be made insignificant for reasonable reaction times.

An example of preliminary nonisobaric studies is given in Figure 2. A 40 mg sample of a bituminous coal, sized to approximately 80 μm average particle size and previously washed with pentane, was packed into a 75 μL cell for these experiments. The extraction temperature was 280°C and the solvent was a 95% n-pentane-5% 2-propanol mixture; thus the temperature was maintained well above the estimated critical temperature of the solvent mixture. The "gentle" CI conditions result in little molecular fragmentation and a dominant protonated molecular ion, greatly simplifying mass spectral interpretation. The experiment shown in Figure 2 involved an initial 2 hr period at 10 atms after which the pressure was increased at a rate of 0.4 atm/min between 10 atm and 100 atm. Figure 2 gives reconstructed single ion profiles for several typical ions in the mass spectra and the total ion current (TIC) or extraction profile, which serve to illustrate the solubility of extractable components as a function of pressure. Large groups of compounds are clearly extracted in the 10-13 atm and 25-28 atm ranges and similar results showing greater structure are obtained with slower pressure ramps. Between 40 and 80 atms a large amount of complex higher molecular weight material is extracted. Mass spectra for these conditions show that species having molecular weights extending to over 1400 are extracted[1]. These results demonstrate the potential for direct mass spectrometric monitoring of supercritical fluid extraction of coal and other related processes. Initial experiments show significant structure in the extraction profiles, suggesting that the potential exists to readily alter the extracted product slate and to obtain significant product fractionation. Approximately 20% of the coal is extracted under these conditions, in reasonable agreement with previous studies.

An example of the application of DFI-MS for fuel characterization is given in Figures 3 and 4. These figures give DFI-mass spectra for four fractions of two diesel fuel marine (DFM) samples, obtained by an alumina column fractionation method, which has been described previously[4]. These DFM samples, designated 81-5 and 81-6, represent a typical fuel (81-5) and a fuel which has been determined to exhibit considerable instability and particulate formation (81-6). The first two (less polar) fractions (A-1 and A-2) contain materials which appear to be nearly totally soluble in supercritical carbon dioxide (34°C, 450 atmospheres), and mass spectra representative of the mixtures are obtained (Figure 3). In contrast, however, the more polar A-3 and A-4 fractions exhibit very limited solubility in supercritical CO_2. Good spectra are obtained, however, in supercritical ammonia (134°C, 400 atmospheres). Since these spectra were obtained using relatively "gentle" chemical ionization reagents (isobutane for the A-1 and A-2 fractions and ammonia for the A-3 and A-4 fractions) only limited ionic fragmentation is anticipated in the spectra, with domination by the protonated molecular ion, $(M+1)^+$. Thus, the DFI mass spectra provide a good measure of the molecular weight distribution of these materials. Comparison of the two relatively non-polar fractions, A-1 and A-2, indicates these fractions, which account for the bulk of the DFM, are quite similar. In contrast, however, comparison of the polar fractions (the A-3 and more polar A-4 fraction) indicates that fuels having greater instability have significantly greater contributions in the 150 to 300 molecular weight region in the A-3 fraction, and substantial contribution in the 300 to 500 molecular weight region, essentially absent for more stable fuel. These results are consistent with the greater amount of material observed in these fractions for the unstable DFM and with the gas chromatography results for the portions which are chromatographable. Research is presently in progress to apply supercritical fluid chromatography techniques using more polar fluids for separation of these materials, in conjunction with analysis by on-line DFI-MS. The much higher chromatographic efficiencies possible with SFC, in conjunction with DFI-MS analysis, promises significant advances for characterization of fuels and coal-derived materials.

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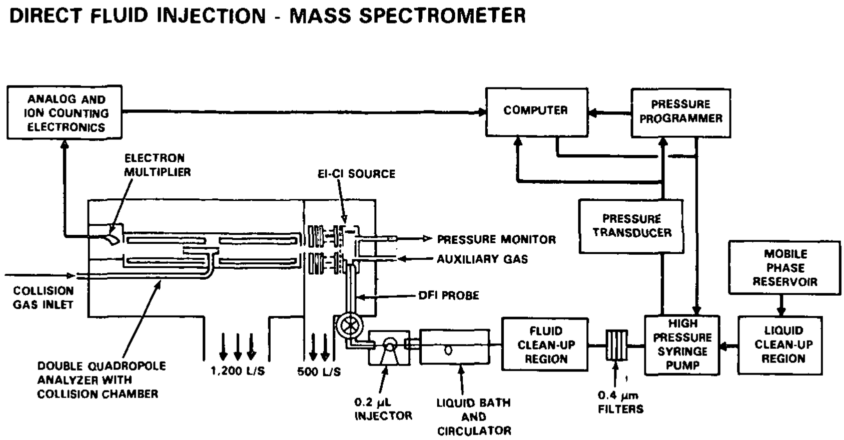

FIGURE 1. Schematic Illustration of the Direct Fluid Injection-Mass Spectrometer. Similar Instrumentation is Used for SFC-MS and Direct Supercritical Fluid Extraction Studies.

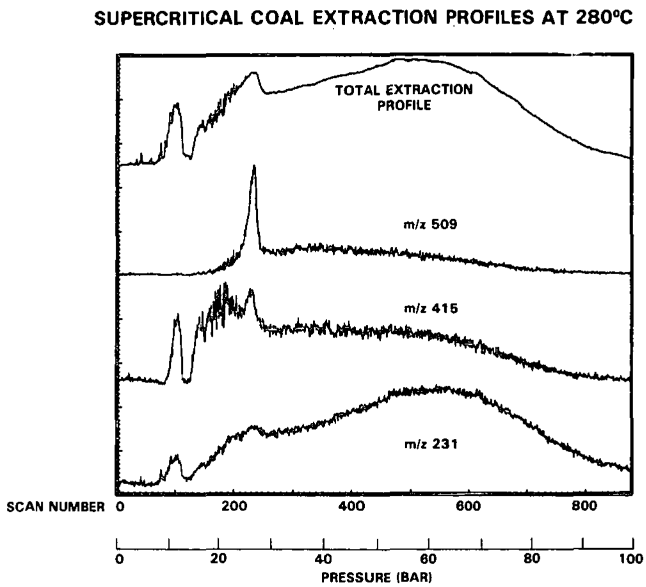

FIGURE 2. Selected Ion Profiles and Total Extraction Profile for a Nonisobaric Supercritical Fluid Coal Extraction Study Using a 95% Pentane-5% 2-Propanol at 280°C.

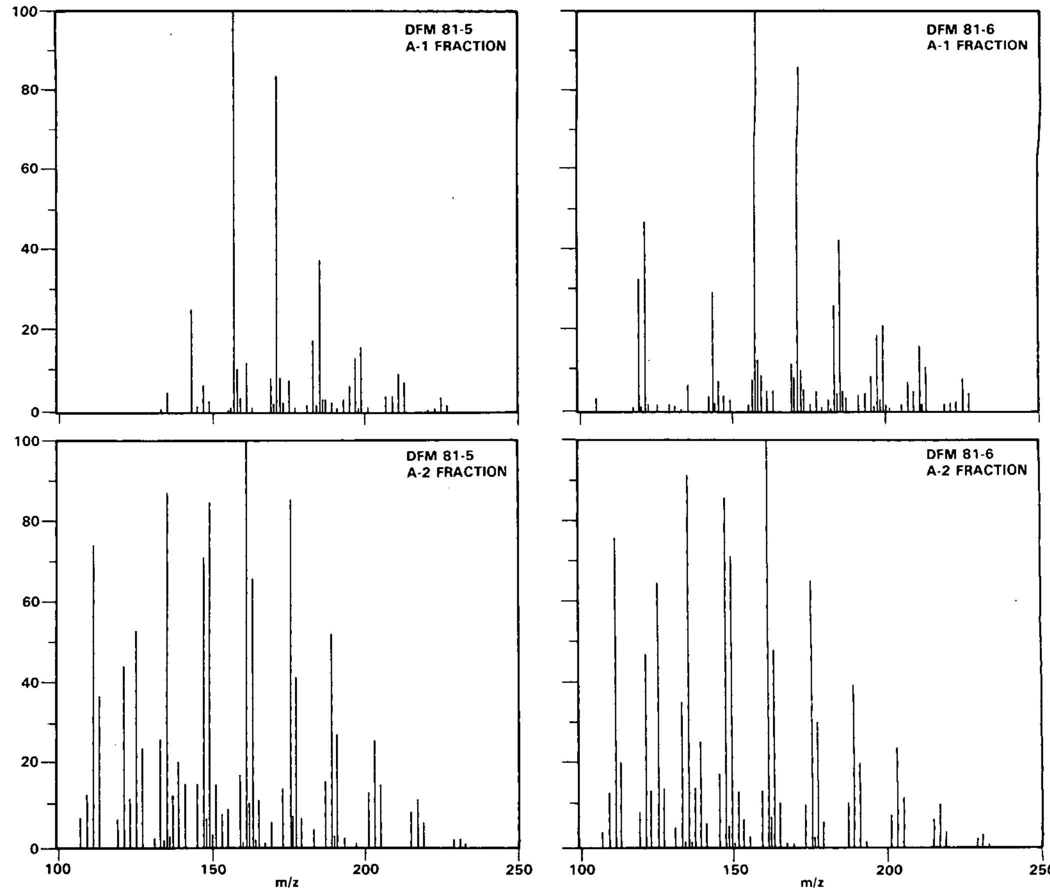

FIGURE 3. DFI-Mass Spectra Using Supercritical CO_2 for the A-1 and A-2 Fractions of Two Diesel Fuel Marine Samples.

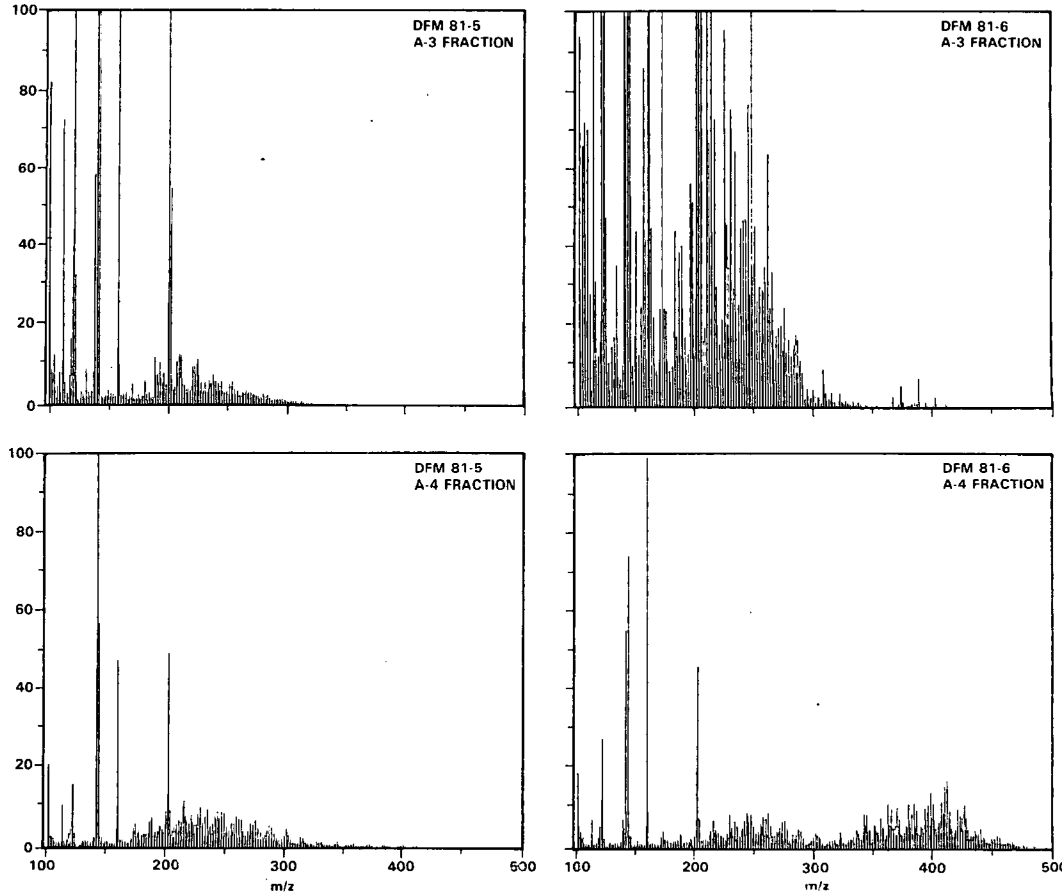

FIGURE 4. DFI-Mass Spectra Using Supercritical NH_3 for the A-3 and A-4 Fraction of Two Diesel Fuel Marine Samples.